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Synopsis

Segmental chain dynamics in polymer blends is a very important topic, not only from a fundamental point of view but also from technological applications. Because of the difficulties in the commercialization of new polymers, industries have turned increasingly towards blending of polymers to optimise their end use (mechanical, rheological) properties. The design of tailor-made materials would be enormously facilitated by the understanding of the blending phenomena at a molecular level. The key question to address is to understand the dynamics of each component of the blend modified by blending? The thesis has systematically studied the effect of multiwalled carbon nanotubes on the chain dynamics, demixing temperature, structural properties and evolution of morphology in a classical miscible polymer blend system (PVDF/PMMA).

The thesis comprises of six chapters, **Chapter 1** is an introductory chapter that outlines the fundamentals of polymer blends, crystallisation in polymer blends and the basics of dielectric spectroscopy. As one of the rationales of this work is to systematic study whether phase separated in these blends can be used as a tool to develop membrane for water purification. This chapter also gives an overview of the reported studies of ultrafiltration membrane fabrication, factors affecting membrane morphology and flux. In **Chapter 2**, the materials and methodology used to carry out experiments and the experimental procedures are discussed.

Chapter 3 discusses the effect of concentration of PMMA and amine functionalized multiwalled carbon nanotubes (MWNTs) on the crystallisation induced phase separation using FTIR, XRD, POM and shear rheology. Electron microscopy and selective etching confirmed the localisation of MWNTs in the PVDF phase of the blends. Blends with MWNTs facilitated in heterogeneous nucleation manifesting in an increase in crystallisation temperature. The crystallisation induced phase separation in PVDF/PMMA blends was observed to influence the interconnected network of MWNTs in the blends.

Chapter 4 discuss the effect of concentration of PMMA and MWNTs on the miscibility and the segmental relaxations was probed *in situ* by DSC and dielectric relaxation spectroscopy (DRS). The dynamic heterogeneity in the blends as manifested by the presence of an extra relaxation at a higher frequency at or below the crystallisation induced phase separation temperature was also discussed. We found that PVDF/PMMA blend (PVDF $\geq$ 80 wt%) exhibits three distinct relaxations; α_c corresponding to crystalline PVDF, $\alpha\beta$ segmental relaxation of PMMA and α_m of amorphous miscibility whereas all relaxations overlap and constitute a single broad relaxation in PVDF/PMMA blend (PVDF $\leq$ 70 wt%). This confirms that there is a certain composition width in this blend wherein three distinct relaxations can be traced. This could due to many reasons like the width of crystal-amorphous interphase in the crystal lamellae, crystal size and morphology is strongly contingent on the concentration of PMMA. Relaxations are not very distinct in presence of MWNTs due to defective spherulites that shift the relaxations towards a higher frequency.

Chapter 5 has attempted to tune the microporous morphology of PVDF membranes using crystallisation induced phase separation in PVDF/PMMA blends. As PVDF/PMMA is a melt-miscible blend, the samples were allowed to crystallise and the amorphous PMMA phase, which isolates in the interlamellar or inter-spherulitic regions in the blends, was etched out to generate microporous structures. The pore sizes can be tuned by varying the PMMA concentration in the blends. We observed that 60/40 PVDF/PMMA blends showed larger pores as compared to 90/10 PVDF/PMMA blends. We further modified PVDF membranes by sputtering silver on the surface. The bacterial cell viability was distinctly suppressed (99 %) in silver sputtered membranes. The ICP analysis suggests that slow Ag^+ ions release from the sputtered membrane surface assisted in developing antibacterial surface. Our findings open new avenues in designing water filtration membranes and also help in understanding the crystallisation kinetics for tuning pore size in membranes.

Chapter 6 summarises the important results of this work. MWNTs act as hetero nucleating agent and specifically interact with PVDF thereby influences the dynamics of PVDF chains. MWNTs can also restrict the amorphous segmental mobility and can influence the intermolecular cooperativity and coupling. The crystallisation induced phase separation in various blends can result in various crystalline morphologies depending on the PVDF concentration. By selectively etching PMMA from the phase-separated blends, microporous morphology can be generated.